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(54) Title: PRODUCTION OF METHANOL FROM HYDROCARBONACEOUS FEEDSTOCK (57) Abstract A hydrogen rich gas is produced from hydrocarbonaceous feedstock by subjecting the feedstock to catalytic partial oxidation under temperature and steam conditions avoiding production of free carbon, thereby producing a synthesis gas containing hydrogen, carbon monoxide and carbon dioxide; converting carbon monoxide to carbon dioxide by water gas shift reaction; and removing carbon dioxide.		

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PRODUCTION OF METHANOL FROM HYDROCARBONACEOUS FEEDSTOCK

Field of the Invention

The invention relates to the production of a hydrogen containing gas from hydrocarbonaceous feedstock. In particular, the invention relates to the preparation of hydrogen containing gas by a process which involves the catalytic partial oxidation of hydrocarbonaceous feedstocks to produce hydrogen-rich synthesis gas, which is further processed to remove non-hydrogen components.

Description of the Prior Art

Hydrocarbonaceous feedstocks, such as natural gases recovered from sites near petroleum deposits, are a convenient source of hydrogen. Typically, such gases contain, as their major constituents, methane, ethane, propane and butane. They may also include low-boiling liquid hydrocarbons. Hydrocarbonaceous feedstock can be converted to hydrogen by first converting it into a synthesis gas containing a major amount of hydrogen, together with minor amounts of carbon monoxide, carbon dioxide and methane. The synthesis gas is treated to remove carbon oxides, residual methane and nitrogen (if present) to produce a gas consisting essentially of hydrogen.

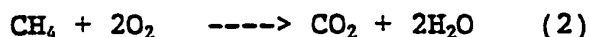
The most commonly employed method for converting hydrocarbonaceous feedstocks to synthesis gas has been catalytic steam reforming. Steam reforming involves an endothermic reaction exemplified for methane by the equation:



In this process, the hydrocarbonaceous feedstock is reacted with steam in the presence of a catalyst, usually a nickel-containing catalyst, at a temperature between about 1200°F (650°C) and 1900°F (1040°C). The hydrocarbons react with steam under these conditions to produce carbon monoxide and hydrogen. Catalytic steam reforming is an expensive process to carry out. Not only is the steam reformer and its nickel-containing catalyst very expensive, but also, the reactions are highly endothermic. Consequently, a great deal of energy must be provided to drive the reaction.

Occasionally, air or oxygen is provided to the reforming reaction in order to provide energy through partial oxidation of hydrocarbons. Air or oxygen reforming is usually performed as a secondary reforming step to reduce unreacted methane (methane slippage) to less than one percent by volume. Upon exiting the primary steam reformer, the unreacted methane is converted in the secondary steam reformer by the injection of air or oxygen, whereby the heat of reaction is supplied by the combustion of methane, hydrogen and carbon monoxide.

Synthesis gas production may also be carried out autothermally in an autothermal reactor by adding an oxidant such as air. The endothermic heat of reaction is supplied by the exothermic combustion reactions:



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The autothermal reactor typically consists of two catalyst beds, the first bed providing a high outlet temperature sufficient for steam reforming in the second bed. Alternatively, the reactants can be partially reformed in a steam reforming furnace and enter the autothermal reactor at a temperature sufficiently high to ignite spontaneously with the entering oxygen, thus producing a higher temperature sufficient for reforming in the downstream catalyst bed. Autothermal reforming generally takes place at relatively low throughputs. The process is carried out at space velocities on the order of 8,000 hr⁻¹ to 12,000 hr⁻¹. "Space velocity" can be defined as the volumetric hourly rate of throughput per volume of catalyst. All figures quoted herein refer to the volumetric hourly rate at standard conditions of temperature and pressure. A disadvantage of the autothermal reforming procedure for hydrogen production is that it consumes a portion of the generated hydrogen in the combustion reaction that is used to provide the heat of reaction for reforming.

The foregoing procedures for producing synthesis gas have the drawbacks of requiring expensive catalysts; large volumes of catalyst; relatively low rates of throughput; equipment that is expensive and, in some cases, takes up excessive amounts of space; and, in some cases, requires unacceptably large amounts of energy to drive the process.

Partial oxidation of hydrocarbonaceous feedstocks represents one alternative to steam reforming in the production of synthesis gas. Most of the partial oxidation processes that have been employed commercially are non-catalytic processes. Non-catalytic partial

oxidation reactions however, are relatively inefficient. They operate at high temperatures, i.e., in the range of 2,200°F (1200°C) to 2,800°F (1540°C) and require large amounts of oxygen. Typically, the oxygen-to-carbon ratio required in non-catalytic partial oxidation is greater than 0.8:1 and often greater than 1:1. Furthermore, free carbon is produced which is removed in a later step.

U.S. Patent 4,390,347 issued to Dille et al. describes a process for the production of synthesis gas by the non-catalytic partial oxidation of a liquid hydrocarbonaceous fuel. The hydrocarbonaceous feedstock is reacted with a free oxygen-containing gas in the presence of steam at an autogenously maintained temperature within the range of 1700°F (930°C) to 3000°F (1650°C) at a pressure in the range of about 1 to 23 atmospheres (1 to 23 bar) absolute. The oxygen-to-carbon molar ratio is said to be from 0.7:1 to 1.5:1.

U.S. Patent 3,890,113 issued to Child et al, describes the production of a methane-rich stream in which non-catalytic partial oxidation of a hydrocarbonaceous feedstock is carried out in the presence of steam and oxygen. The ratio of free oxygen in the oxidant to carbon in the feedstock is in the range of 0.8:1 to 1.5:1. The product synthesis gas is subjected to a water gas shift reaction to increase the amount of hydrogen in the gas.

U.S. Patent 3,927,998 issued to Child et al., relates to the production of a methane rich stream by the partial oxidation of a hydrocarbonaceous fuel employing a steam to fuel weight ratio of 2.2:1 to 2.9:1 and an oxygen-to-carbon molar ratio of 0.8:1 to 0.84:1. The partial oxidation is carried out in the

absence of catalysts. The synthesis gas is cooled and water, carbon dioxide, carbon and other impurities are removed. The hydrogen and carbon monoxide in the gas are reacted in a catalytic methanation zone to produce a methane-rich stream.

Conversion efficiency of oxidation processes can generally be improved by the use of catalysts; but where the oxidation process is only partial, i.e. with insufficient oxygen to completely oxidize the hydrocarbon, then the catalyst is subject to carbon deposit and blockage. Carbon deposits can be avoided by using expensive catalyst materials in generally uneconomical processes. For example, U.S. Patent 4,087,259, issued to Fujitani et al., describes employment of a rhodium catalyst in a process wherein liquid hydrocarbonaceous feedstock is vaporized and then partially oxidized in contact with the rhodium catalyst at a temperature in the range of 690° to 900°C with optional steam added as a coolant at rate not more than 0.5 by volume relative to the volume of the liquid hydrocarbon in terms of the equivalent amount of water. The rhodium catalyst enables partial oxidation without causing deposition of carbon, but at temperatures greater than 900°C, thermal decomposition ensues producing ethylene or acetylene impurities. When steam is added, the quantity of hydrogen produced is increased while the yield of carbon monoxide remains constant due to catalytic decomposition of the steam to hydrogen gas and oxygen. A "LHSV" (Liquid Hourly Space Velocity) from 0.5 to 25 l/hour is disclosed; particularly, a high yield from partial oxidation of gasoline vapor, without steam, is produced at a temperature of 725°C and at a LHSV of 20, and with

steam, is produced at temperatures of 700°C and 800°C and at a LHSV of 2.

In order to obtain acceptable levels of conversion using catalytic partial oxidation processes of the prior art it has been necessary to use space velocities
5 below about 12,000 hr⁻¹. For example, U.S. Patent No. 4,522,894, issued to Hwang et al., describes the production of a hydrogen-rich gas to be used as fuel for a fuel cell. The process reacts hydrocarbon feed
10 with steam and an oxidant in an autothermal reformer using 2 catalyst zones. The total hourly space velocity is between 1,960 hr⁻¹ and 18,000 hr⁻¹. Because the prior art processes must be carried out at low space velocity, catalytic partial oxidation reactors of
15 the prior art have had to have large catalyst beds in order to achieve the throughputs desired in commercial operation. This increases the size and cost of the partial oxidation reactor.

It is an object of the present invention to
20 provide a process for the production of a hydrogen rich gas from hydrocarbonaceous feedstock which is energy efficient, is capable of using low cost catalysts and employs relatively small equipment volume to achieve commercially acceptable throughput.

25 It is a further object of the invention to provide a process for the production of a hydrogen rich gas from hydrocarbonaceous feedstock with a relatively low oxygen demand, thereby increasing throughput of hydrocarbonaceous feed.

30 These and other objects of the invention are achieved by a process which is described below.

Summary of the Invention

The invention provides a process for producing hydrogen from hydrocarbonaceous feedstocks in which the feedstock is converted into hydrogen by a process scheme which is highly cost efficient and utilizes
5 equipment that is less costly and space-consuming than that employed in prior art processes.

This invention provides a process for the production of a hydrogen rich gas in which
hydrogen-rich synthesis gas is generated by the
10 catalytic partial oxidation of a hydrocarbonaceous feedstock such as natural gas with an oxidant stream that is preferably oxygen-rich under temperature and steam conditions avoiding production of free carbon; converting the carbon nonoxide in the synthesis gas to
15 carbon dioxide by subjecting the synthesis gas to a water shift gas reaction; removing carbon dioxide from the gas stream; and recovering hydrogen-rich gas.

In one embodiment, the invention provides a process for producing hydrogen from hydrocarbonaceous
20 feedstock which comprises:

- (a) introducing to a catalytic partial oxidation zone an essentially completely mixed gaseous mixture of a hydrocarbonaceous feedstock, oxygen or an oxygen-containing gas and,
25 optionally, steam in which the steam-to-carbon molar ratio is from 0:1 to 4.0:1 and the oxygen-to-carbon molar ratio is from 0.4:1 to 0.8:1, said mixture being introduced to the catalytic partial oxidation
30 zone at a temperature not lower than 200°F (93°C) below its catalytic autoignition temperature;
- (b) partially oxidizing the hydrocarbonaceous feedstock in the catalytic partial oxidation

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- 5 zone under temperature and steam conditions
avoiding formation of free carbon by passing
the mixture through a catalyst capable of
catalyzing the partial oxidation of the
hydrocarbons, said catalyst having a ratio of
geometric surface area to volume of at least
5 cm²/cm³ and a volume corresponding to a
space velocity of between 20,000⁻¹ and
500,000⁻¹, thereby producing synthesis gas
10 containing hydrogen, carbon monoxide and
carbon dioxide;
- (c) separating hydrogen in the synthesis gas to
produce a hydrogen product stream.

Brief Description of the Drawings

15 Fig. 1 is an elevated cross-section view of a
reactor having at its input a mixer and distributor
suitable for introducing the reactants to the catalyst
bed.

20 Fig. 2 is an enlarged elevational cross-section
view of a broken-away portion of the mixer and
distributor of Fig. 1.

Fig. 3 is a top view of a broken-away quarter
section of the mixer and distributor of Fig. 1.

25 Fig. 4 is a bottom view of a broken-away quarter
section of the mixer and distributor of Fig. 1.

Fig. 5 is a diagrammatic elevational
cross-sectional illustration of a broken-away portion
of the mixer and feeder of Figs. 1 and 2 showing
critical dimensions.

30 Fig. 6 is a flow diagram in schematic form
illustrating a process of the invention for hydrogen
production.

Fig. 7 is a graph plotting oxygen-to-carbon molar ratio vs. steam-to-carbon molar ratio for three different operating temperatures at an operating pressure of 400 psig (2760 KPa).

5 Fig. 8 is a graph plotting the hydrogen-to-carbon monoxide molar ratio in the catalytic partial oxidation reaction product vs. the steam-to-carbon molar ratio for three different operating temperatures at an operating pressure of 400 psig (2760 KPa).

10 Fig. 9 is a graph plotting the volume % methane in the catalytic partial oxidation product vs. the steam-to-carbon molar ratio for three different operating temperatures at an operating pressure of 400 psig (2760 KPa).

15 Fig. 10 is a graph plotting the volume % carbon dioxide in the catalytic partial oxidation product vs. the steam-to-carbon molar ratio for three different operating temperatures at an operating pressure of 400 psig (2760 KPa).

20 Fig. 11 is a graph plotting the molar ratio of total hydrogen and carbon monoxide in the product to total hydrogen and carbon in the feedstock vs. the steam-to-carbon molar ratio for three different operating temperatures at an operating pressure of 400 psig (2760 KPa).

25 Fig. 12 is a process flow diagram of a hydrogen producing plant using catalytic partial oxidation in accordance with the invention.

Detailed Description of the Preferred Embodiments

30 The process of the present invention can be used to produce hydrogen from any gaseous or low-boiling hydrocarbonaceous feedstock. Typically, the

hydrocarbonaceous feedstock is a gas containing principally methane, such as natural gas having the following approximate composition: methane, 93%; ethane, 5%; propane 1.5%; butane and higher hydrocarbons, 0.5%.

In general, the process of the invention involves the steps of catalytic partial oxidation of hydrocarbonaceous feedstock at a space velocity in the range from 20,000 hour⁻¹ to 500,000 hour⁻¹ under temperature and steam conditions avoiding production of free carbon to produce synthesis gas; treatment of the resultant synthesis gas to remove components other than hydrogen (e.g., carbon oxides) and to recover a carbon dioxide stream; and recovery of a hydrogen-rich gas. Preferred methods for carrying out these steps are described below.

Catalytic Partial Oxidation

The catalytic partial oxidation of hydrocarbonaceous feedstock is carried out according to a process described in copending, commonly assigned U.S. application Serial No. 085,160 filed August 14, 1987 in the names of M. Dunster and J.D. Korchnak.

One particular aspect of the invention is the substantial capital cost savings and/or advantageous operating economy resulting from the employment of catalytic partial oxidation to produce the raw synthesis gas employed in the hydrogen producing process. This is made possible by the discovery that catalytic partial oxidation performed at a temperature, as measured at the exit of the catalytic reaction zone, equal to or greater than a minimum non-carbon-forming temperature selected as a linear function which includes a range from 1600°F (870°C) to 1900°F (1040°C) corresponding to a range of the steam-to-carbon molar

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ratio from 0.4:1 to 0:1 and at a space velocity in the range from 20,000 hour⁻¹ to 500,000 hour⁻¹ produces essentially no free carbon deposits on the catalyst. Further, it is found that products of the partial catalytic oxidation in the process of the invention consist essentially of hydrogen, carbon monoxide and carbon dioxide at oxidation temperatures equal to or greater than the minimum temperature, rhodium catalysts are not required to prevent carbon formation. For example in Fig. 7, dotted line 25 represents a generally linear function which, at a steam/carbon ratio of 0, corresponds to a minimum partial oxidation temperature of about 1900°F (1040°C), and at a steam/carbon ratio of 0.4 corresponds to a minimum partial oxidation temperature of about 1600°F (870°C); favorable catalytic partial oxidation without producing free carbon occurs at temperatures and steam/carbon ratios equal to or greater than points on the line. Further, lower minimum temperatures at corresponding steam/carbon ratios greater than 0.4 can be extrapolated from the linear function represented by line 25.

In the catalytic partial oxidation step of the process of the invention, reactant gases are introduced to the catalytic partial oxidation reaction zone, i.e. the catalyst bed, at an inlet temperature not lower than 200°F (93°C) below the catalytic autoignition temperature of the feed mixture. Preferably the reactant gases are introduced at a temperature at or above the autoignition temperature of the mixture. The reactants should be completely mixed prior to the reaction. Introducing the thoroughly mixed reactant gases at the proper temperature ensures that the partial oxidation reactions will be mass transfer

controlled. Consequently, the reaction rate is relatively independent of catalyst activity, but dependent on the surface-area-to-volume ratio of the catalyst. It is possible to use any of a wide variety of materials as a catalyst, provided that the catalyst has the desired surface-area-to-volume ratio. It is not necessary that the catalyst have specific catalytic activity for steam reforming. Even materials normally considered to be non-catalytic can promote the production of synthesis gas herein when used as a catalyst in the proper configuration. The term "catalyst", as used herein, is intended to encompass such materials.

The catalytic partial oxidation step can be understood with reference to the figures. The catalytic partial oxidation zone is typically the catalyst bed of a reactor such as that illustrated in Fig. 1. As shown in Fig. 1, a reactor 100 for partially oxidizing a gaseous feedstock includes an input mixing and distributor section indicated generally at 30. The mixer and distributor 30 mixes the feedstock with an oxidant and distributes the mixture to the entrance of a catalytic reactor section indicated generally at 32 wherein the feedstock is partially oxidized to produce a product which is then passed through the exit section indicated generally at 34.

The reactor includes an outer shell 40 of structural metal such as carbon steel with a top 42 secured thereon by bolts (not shown) or the like. A layer 43 of insulation, such as 2300°F (1260°C) BPCF ceramic fiber insulation, is secured to the inside of the upper portion of the shell 40 including the top 42. In the lower portion of the mixing section 30, in

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the reactor section 32 and outlet section 34, there are secured layers 46, 48 and 50 on the inside of the shell. The layer 46 is a castable or equivalent insulation such as 2000°F (1090°C) ceramic insulation. 5 The layer 48 is also a castable or equivalent layer of insulation but containing 60% alumina for withstanding 3000°F (1650°C). The internal layer 50 is a refractory or equivalent layer such as 97% alumina with ceramic anchors or 97% alumina brick for withstanding the 10 interior environment of the reactor section.

The catalytic reactor section 32 contains one or more catalyst discs 54. As shown, the reactor contains a sequence of discs 54 separated by high alumina rings 58 between each adjacent pair of discs. The stack is 15 supported by a grill with high alumina bars 56. A sample port 60 is formed in the lower end of the reaction section and has a tube, such as type 309 stainless steel tube 62, extending below the bottom refractory disc 54 for withdrawing samples of the 20 product.

The outlet section 34 is suitably formed for being connected to a downstream heat recovery boiler (not shown) and/or other processing equipment.

The catalyst comprises a high surface area 25 material capable of catalyzing the partial oxidation of the hydrocarbonaceous feedstock. The catalyst is in a configuration that provides a surface area to volume ratio of at least 5 cm²/cm³. Preferably, the catalyst has a geometric surface area to volume ratio of at 30 least 20 cm²/cm³. While there is no strict upper limit of surface area to volume ratio, it normally does not exceed about 40 cm²/cm³.

The catalyst disc 54 can be, for example, a monolithic structure having a honeycomb type

cross-sectional configuration. Suitable monolithic structures of this type are produced commercially, in sizes smaller than those used in the process of the invention, as structural substrates for use in the catalytic conversion of automobile exhausts and as catalytic combustion chambers of gas turbines or for catalytic oxidation of waste streams. Typically, the monolithic structure is an extruded material containing a plurality of closely packed channels running through the length of the structure to form a honeycomb structure. The channels are typically square and may be packed in a density as high as 1,200 per square inch (190 per cm_2) of cross section. The monolithic structure can be constructed of any of a variety of materials, including cordierite ($\text{MgO}/\text{Al}_2\text{O}_3/\text{SiO}_2$), Mn/MgO-cordierite ($\text{Mn-MgO}/\text{Al}_2\text{O}_3/\text{SiO}_2$), mullite ($\text{Al}_2\text{O}_3/\text{SiO}_2$), mullite aluminum titanate ($\text{Al}_2\text{O}_3/\text{SiO}_2-(\text{Al},\text{Fe})_2\text{O}_3/\text{TiO}_2$), zirconia spinel ($\text{ZrO}_2/\text{MgO}/\text{Al}_2\text{O}_3$), spinel ($\text{MgO}/\text{Al}_2\text{O}_3$), alumina (Al_2O_3) and high nickel alloys. The monolithic catalyst may consist solely of any of these structural materials, even though these materials are not normally considered to have catalytic activity by themselves. Using honeycombed substrates, surface area to volume ratios up to $40 \text{ cm}^2/\text{cm}^3$ or higher can be obtained. Alternatively, the monolithic substrate can be coated with any of the metals or metal oxides known to have activity as oxidation catalysts. These include, for example, palladium, platinum, rhodium, irridium, osmium, ruthenium, nickel, chromium, cobalt, cerium, lanthanum and mixtures thereof. Other metals which can be used to coat the catalyst disc 54 include noble metals and metals of groups IA, IIA, III, IV, VB, VIB, or VIIB of the periodic table of elements.

The catalyst discs 54 may also consist of structural packing materials, such as that used in packing absorption columns. These packing materials generally comprise thin sheets of corrugated metal tightly packed together to form elongate channels running therethrough. The structural packing materials may consist of corrugated sheets of metals such as high temperature alloys, stainless steels, chromium, manganese, molybdenum and refractory materials. These materials can, if desired, be coated with metals or metal oxides known to have catalytic activity for the oxidation reaction, such as palladium, platinum, rhodium, irridium, osmium, ruthenium, nickel, chromium, cobalt, cerium, lanthanum and mixtures thereof.

The catalyst discs 54 can also consist of dense wire mesh, such as high temperature alloys or platinum mesh. If desired, the wire mesh can also be coated with a metal or metal oxide having catalytic activity for the oxidation reaction, including palladium, platinum, rhodium, irridium, osmium, ruthenium, nickel, chromium cobalt, cesium, lanthanum and mixtures thereof.

The surface area to volume ratio of any of the aforementioned catalyst configurations can be increased by coating the surfaces thereof with an aqueous slurry containing about 1% or less by weight of particulate metal or metal oxide such as alumina, or metals of groups IA, IIA, III, IV, VB, VIB and VIIB and firing the coated surface at high temperature to adhere the particulate metal to the surface, but not so high as to cause sintering of the surface. The particles employed should have a BET (Brunnauer-Emmett-Teller) surface area greater than about 10 m²/gram, preferably greater than about 200 m²/gram.

In the practice of the invention, a gaseous mixture of hydrocarbonaceous feedstock, oxygen or an oxygen-containing gas, which can be air, oxygen-enriched air, or other oxygen-rich gas, and, optionally, steam is introduced into the catalytic partial oxidation zone at a temperature not lower than 200°F (93°C) below its autoignition temperature. Preferably, the oxidant is an oxygen-rich gas. The term "oxygen-rich gas" as used herein refers to a gas containing at least 70 mol. % oxygen, preferably at least 90 mol. % oxygen, and which can be pure oxygen. Preferably, the gaseous mixture enters the catalytic partial oxidation zone at a temperature equal to or greater than its autoignition temperature. It is possible to operate the reactor in a mass transfer controlled mode with the reactants entering the reaction zone at a temperature somewhat below the autoignition temperature since the heat of reaction will provide the necessary energy to raise the reactant temperature within the reaction zone. In such a case, however, it will generally be necessary to provide heat input at the entrance to the reaction zone, for example by a sparking device, or by preheating the contents of the reactor, including the catalyst, to a temperature in excess of the autoignition temperature prior to the introduction of the reactants to initiate the reaction. If the reactant temperature at the input to the reaction zone is lower than the autoignition temperature by more than about 200°F (93°C), the reaction becomes unstable.

When the reactant mixture enters the catalytic partial oxidation zone at a temperature exceeding its autoignition temperature, it is necessary to introduce the mixture to the catalyst bed immediately after

mixing; that is, the mixture of hydrocarbonaceous feedstock and oxidant should preferably be introduced to the catalyst bed before the autoignition delay time elapses. It is also essential that the gaseous reactants be thoroughly mixed. Failure to mix the reactants throughly reduces the quality of the product and can lead to overheating. A suitable apparatus for mixing and distributing the hydrocarbonaceous feedstock and oxygen or oxygen-containing gas so as to provide thorough mixing and to introduce the heated reactants into the reaction zone in a sufficiently short time is illustrated in Figs. 1-5 and described in more detail in copending commonly assigned patent Application Serial No. 085,159, filed August 14, 1987 in the names of J.D. Korchnak, M. Dunster, and J.H. Marten.

Referring to Fig. 1, one of the feed gas, i.e. hydrocarbonaceous gas or oxygen-containing gas, is introduced into the input section 30 through a first inlet port 66 through the top 42 which communicates to an upper feed cone 68 which forms a first chamber. The cone 68 is fastened by supports 69 in the top 42. The other feed gas is introduced into the input section 30 through second inlets 70 extending through side ports of the shell 40 and communicating to a second chamber 72 which is interposed between the upper chamber 68 and the inlet of the catalyst reaction section 32. A ring 73 mounted on the central portion of an upper wall 75 of the chamber 72 sealingly engages the lower edge of the cone 68 so that the wall 82 forms a common wall between the upper chamber 68 and lower chamber 72. The chamber 72 has an upper outer annular portion 74, see also Figs. 2 and 3, which is supported on the top surface of the refractory layer 50. A lower portion of the chamber 72 has a tubular wall 76 which extends

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downward in the refractory sleeve 50. The bottom of the chamber 76 is formed by a cast member 78.

Optionally, steam can be introduced into either or both of the hydrocarbonaceous feedstock and oxygen or oxygen-containing gas. The gases are fed to the reactor in relative proportions such that the steam-to-carbon molar ratio is in the range from 0:1 to 4.0:1, is preferably in the range from 0.8:1 to 3.0:1, and is most preferably in the range from 1.0:1 to 2.0:1. The oxygen-to-carbon ratio is in the range from 0.4:1 to 0.8:1 and is preferably in the range from 0.45 to 0.65.

The reactant mixture preferably enters the catalytic reactor section 32 at a temperature at or above its autoignition temperature. Depending on the particular proportions of reactant gases, the reactor operating pressure and the catalyst used, this will generally be between about 550°F (288°C) and 1,100°F (593°C). Preferably, hydrocarbonaceous feedstock and steam are admixed and heated to a temperature in the range from 650°F (343°C) to 1,200°F (650°C) prior to passage through inlet port(s) 70 or 66. Oxygen or oxygen-containing gas, such as air, is heated to a temperature in the range from 150°F (65°C) to 1200°F (650°C) and passes through the other inlet port(s) 66 or 70.

Referring to Fig. 2, the mixing and distributing means comprises a plurality of elongated tubes 80 having upper ends mounted in the upper wall 75 of the chamber 72. The lumens of the tubes at the upper end communicate with the upper chamber 68. The bottom ends of the tubes 80 are secured to the member 78 with the lumens of the tubes communicating with the upper ends of passageways 84 formed vertically through the member

78. Orifices 86 are formed in the walls of the tubes 80 for directing streams of gas from the chamber 72 into the lumens of the tubes 80. The inlets 66 and 70, the cone 68, the supports 69 are formed from a conventional corrosion and heat resistant metal while the chamber 72, tubes 80 and member 78 are formed from a conventional high temperature alloy or refractory type material.

The number of tubes 80, the internal diameter 90 (see Fig. 5) of the tubes 80, the size and number of the orifices 86 in each tube are selected relative to the gas input velocities and pressures through inlets 66 and 70 so as to produce turbulent flow within the tubes 80 at a velocity exceeding the flashback velocity of the mixture. The minimum distance 92 of the orifices 86 from the bottom end of the tube 80 at the opening into the diverging passageways 84 is selected to be equal to or greater than that required for providing substantially complete mixing of the gas streams from chambers 68 and 72 under the conditions of turbulence therein. The size of the internal diameter 90 of the tubes 80 as well as the length 94 of the tubes is designed to produce a sufficient pressure drop in the gas passing from the chamber 68 to the reaction chamber so as to provide for substantially uniform gas flow through the tubes 80 from the chamber 68. Likewise the size of the orifices 86 is selected to provide sufficient pressure drop between the chamber 72 and the interior of the tubes 80 relative to the velocity and pressures of the gas entering through inlets 70 so as to provide substantially uniform volumes of gas flows through the orifices 86 into the tubes 80.

The diverging passageways in the member 78 are formed in a manner to provide for reduction of the velocity of the gas to produce uniform gas distribution over the inlet of the catalyst. The rate of increase of the cross-section of the passageway 84 as it proceeds downward, i.e., the angle 98 that the wall of the passageway 84 makes with the straight wall of the tubes 80, must generally be equal to or less than about 15° and preferably equal to or less than 7° in order to minimize or avoid creating vortices within the passageways 84. This assures that the essentially completely mixed gases, at a temperature near to or exceeding the autoignition temperature, will pass into the catalyst bed in a time preferably less than autoignition delay time. The configuration of the bottom end of the passageways 84, as shown in Fig. 4, is circular.

The catalytic partial oxidation reaction is preferably carried out in the catalytic reaction section 32 at a pressure greater than 100 psig (690 KPa), more preferably at a pressure greater than 250 psig (1720 KPa). Generally the catalytic partial oxidation is performed at a temperature, as measured at the exit of the catalyst, in the range from 1400°F (760°C) to 2300°F (1260°C). Preferably, the catalytic partial oxidation temperature, as measured at the exit, is in the range from 1600°F (870°C) to 2000°F (1090°C). At temperatures below about 1400°F (760°C), reaction times are excessive, and at temperatures above 2300°F (1260°C), the amounts of ethylene and acetylene in the product increase.

Essentially little or no reforming reactions are employed in the process of the invention; that is, the

process of the invention relies essentially solely on partial oxidation and the water gas shift reaction



to convert hydrocarbonaceous feedstock to synthesis gas. Catalytic partial oxidation of uniformly premixed feedstock and oxygen does not require any reforming reactions to take place. The catalyst is selected to promote the partial oxidation reaction, and not

5 necessarily any reforming reaction. The steam reforming reaction (equation 1) generally requires a low space velocity, i.e. generally below about 12,000 hour⁻¹, and the employment of space velocities above 20,000 hour⁻¹ in the present process precludes efficient steam reforming of the feedstock. It is believed that increased hydrogen production, above that attributable solely to partial oxidation, is due more to the water gas shift reaction (equation 5) than to the steam reforming reaction (equation 1).

10 The product gas exiting the outlet section 34 consists essentially of hydrogen, carbon oxides, i.e. carbon monoxide and carbon dioxide, methane, water vapor and any inert components (e.g. nitrogen or argon) introduced with the feedstock or oxidant. Trace amounts of C²- and higher hydrocarbons may be present in the product gas. As used herein "trace amounts" means less than about 0.1% by weight.

Removal of Carbon Oxides

20 The synthesis gas exiting the catalytic partial oxidation zone is cooled to a temperature from about 350°F (175°C) to about 750°F (400°C) using conventional heat exchange methods, either by heating the hydrocarbon and steam feedstock, heating the oxidant stream, superheating steam, raising steam in a boiler, preheating boiler feedwater or a combination thereof.

The first step in the removal of carbon oxides is the conversion of carbon monoxide to carbon dioxide by the water gas shift reaction



- 5 in which carbon monoxide is reacted with water to produce carbon dioxide and hydrogen. The water gas shift reaction is known, and suitable equipment for carrying out the reaction is commercially available. The water gas shift reaction can be carried out in two
- 10 stages, i.e. a high temperature shift and a low temperature shift. In this procedure, the synthesis gas is first reacted with water vapor at a temperature in the range from about 580°F (304°C) to 750°F (400°C) and a pressure in the range from about 10 atm to 40 atm
- 15 (1000 KPa to 4000 KPa), followed by reaction at a temperature in the range from about 350°F (175°C) to 500°F (260°C) and a pressure in the range from about 10 atm to 40 atm (1000 to 4000 KPa). Alternatively the water gas shift reaction can be carried out in a single
- 20 stage, low temperature tubular, steam-raising reactor shift vessel. In this procedure, the water vapor and synthesis gas are reacted at a temperature in the range from about 350°F (175°C) to 500°F (260°C) and a pressure in the range from about 10 atm to 40 atm (1000
- 25 to 4000 KPa). The exit stream from the water gas shift reaction zone has a carbon monoxide content less than about 1.0%.

- Essentially all of the remaining carbon monoxide can be converted to carbon dioxide by catalytic
- 30 selective oxidation. In this procedure, the exit stream from the water gas shift reaction zone, after heat removal to reduce its temperature to a range from about 100°F (38°C) to 250°F (120°C), is reacted with air in the presence of a catalyst that is highly

selective for the oxidation of carbon dioxide under conditions in which little or no hydrogen is oxidized. The catalytic selective oxidation procedure is known in the art and described by U.S. Patents No. 3,216,782, 5 No. 3,216,783 and No. 3,631,073. Suitable process equipment for carrying out the selective oxidation procedure is commercially available for example, under the trademark Selectoxo.

Alternatively to the catalytic selective oxidation 10 procedure, remaining carbon monoxide can be methanated using known procedures. Since methanation reacts each mole of carbon monoxide with three moles of hydrogen, this procedure consumes some of the hydrogen product. This may be acceptable, depending on the end use 15 intended for the product gas.

Any other procedures known in the art for removing carbon monoxide can be employed to remove traces of carbon monoxide from the gas stream.

After conversion of carbon monoxide to carbon 20 dioxide, carbon dioxide is removed from the gas stream and recovered using known procedures such as, for example, passing it through a countercurrent stream of a liquid absorbent medium, such as potassium carbonate, MEA, DEA, etc., which absorbs the carbon dioxide. 25 Commercial processing units for carbon dioxide removal are available for example, under the trademarks Selexol, Amine Guard, and Benfield. These processes absorb the carbon dioxide into a chemical or physical absorption medium at relatively high pressure and low 30 temperature, allowing other gases to pass through essentially unchanged. The chemical or physical absorbent is then regenerated by pressure let down into a lower pressure vessel and, if a chemical absorbent is used, stripped of carbon dioxide by a counter current

stream of steam. The carbon dioxide gas is discharged from the top of the regenerator and the absorbent returned to the absorber to recover more carbon dioxide.

5 Additional Hydrogen Enrichment

Additional steps may be employed to increase the proportion of hydrogen in the product gas. In particular, when air or oxygen-enriched air is used as an oxidant in the catalytic partial oxidation step, the
10 synthesis gas contains nitrogen which can be removed from the product stream.

Any known procedure for removing nitrogen from a gas stream can be employed. A preferred method for removing nitrogen is pressure swing adsorption.

15 Pressure swing adsorption involves the adsorption of components to be removed at high pressure followed by their desorption at low pressure. The process operates on a repeated cycle having two basic steps, adsorption and regeneration. Not all the hydrogen is recovered as
20 some is lost in the waste gas during the regeneration stage. By careful selection of the frequency and sequence of steps within the cycle, however, the recovery of hydrogen can be maximized and the ratio of hydrogen to nitrogen in the product effluent gas can be
25 strictly controlled to give the desired ratio.

Regeneration of the adsorbent is carried out in three basic steps: (a) The adsorber is depressurized to the low pressure. Some of the waste components are desorbed during this step. (b) The adsorbent is purged
30 at low pressure, with the product hydrogen removing the remaining waste components. (c) The adsorber is repressurized to adsorption pressure ready for service.

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The waste gases evolved during regeneration are collected in a waste gas surge drum and then used as fuel.

5 Pressure swing absorption can also be used to remove residual carbon dioxide, methane, water vapor and trace contaminants such as H_2S .

Another suitable method for removing nitrogen from the gas stream is by cryogenic separation, a procedure whereby gases are fractionated according to their
10 liquefaction temperatures. Commercially available cryogenic separators can be employed to remove nitrogen from the gas stream.

Using the procedures of the invention, a hydrogen product stream can be obtained that contains at least
15 75 mol. % hydrogen, preferably at least 90 mol. % hydrogen, and most preferably at least 95 mol. % hydrogen.

The process of the invention is illustrated schematically in a preferred embodiment in the flow
20 diagram of Fig. 6. Hydrocarbonaceous feedstock such as a natural gas is fed, together with steam and oxygen-rich gas, to a catalytic partial oxidation reactor 100 such as illustrated in Fig. 1. The
25 resulting synthesis gas exits the catalytic partial oxidation reactor 100 at a temperature from about 1600°F (870°C) to 1900°F (1040°C) and is passed through a heat exchanger at step 102 to reduce its temperature to between 350°F (175°C) and 750°F (400°C). The gas is
30 then passed to a water gas shift reaction zone 104 where carbon monoxide and water vapor are reacted in contact with a shift catalyst to convert carbon monoxide to carbon dioxide and to produce additional hydrogen. The quantity of gas contacted with the shift catalyst will depend on the required quality of the

product gas stream. If the gas is intended for reducing purposes only, for example, it may be acceptable to eliminate the water gas shift reaction step. The exit gas from the water gas shift reaction zone 104 is passed through a heat exchanger at step 106 to reduce its temperature to between 80°F (27°C) and 200°F (93°C). The gas is then fed to a carbon dioxide removal unit at step 108, where the gas stream is contacted with a countercurrent stream of carbon dioxide absorbent, which absorbs the carbon dioxide from the gas stream. The hydrogen product stream may, if desired, be subjected to further processing steps, for example, nitrogen removal if air is employed in the oxidant stream of the catalytic partial oxidation step 100.

When compared to present day commercial processes, the process of the present invention employing the catalytic partial oxidation route using, as oxidant, a stream containing in excess of 70 mole percent of oxygen, as described herein, offers the following advantages:

1. The high cost steam reforming furnace is eliminated when compared to the conventional commercial route.
2. Low oxygen consumption when compared to conventional partial oxidation.
3. Low water consumption when compared to steam reforming.
4. Low cost when compared to catalytic partial oxidation routes which use air or enriched air to produce a nitrogen rich synthesis gas at the exit of the catalytic partial oxidation reactor.

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5. Reduced area requirement when compared to the steam reforming route (particularly suitable for offshore applications).

5 6. High efficiency when compared to conventional commercial hydrogen production processes and when compared to catalytic partial oxidation using air or enriched air containing less than 70 mole percent of oxygen.

10 7. Lower in capital cost than all present commercial processes.

In another embodiment of a hydrogen producing process in accordance with the invention as illustrated in Fig. 12, a natural gas stream 200 is passed through coil 202 of a fired heater 204 to preheat the
15 hydrocarbonaceous feedstock. The heater 204 is heated by combustion of waste fuel 206 with air stream 208. From the heater 202, the feedstock is fed in line 210 to desulphurization vessel 212. Feedstock desulphurization depends on the quantity and types of
20 sulphur present in the feedstock. Hydrogen sulphide is most economically removed simply by passing the feedstock over a bed of zinc oxide absorbent. The hydrogen sulphide present reacts with the zinc oxide to produce zinc sulphide. The natural gas feedstock 200 is
25 heated to a temperature in the range from 400°F (200°C) to 750°F (400°C) and passed through the zinc oxide absorbent contained in the desulphurization vessel 212 to remove sulfur compounds.

The desulphurized natural gas feedstock 214 is
30 mixed with steam 216 to achieve a steam to carbon molar ratio in the range from 1.0:1 to 1.5:1. The mixture 218 of steam and feedstock is further heated in coil 220 of the heater 204 to approximately 1100°F (590°C) and passed over line 222 to one inlet of the catalytic

partial oxidation (CPO) reactor 100 where the feedstock-steam mixture is thoroughly mixed with oxygen 224 and feed to the catalytic oxidation zone as described above. The main reactions taking place within the CPO reactor 100 are the partial oxidation reactions:



and the water gas shift reaction



as described above. The exit temperature of the effluent 226 from the CPO reactor is approximately 1750°F (954°C).

The reactor effluent 226 is first cooled in CPO boiler 228 by raising steam from water flow from steam drum 229, before being passed through line 230 to water quench evaporator or super cooler 232, and then through line 234 to low temperature shift reactor 236. In order to avoid reducing conditions within the shift reactor 236, which would result in catalyst deterioration by reduction of the shift catalyst and formation of carbon, and methanation of carbon oxides, and also in order to improve carbon monoxide shift conversion, the steam to gas ratio is increased upstream of the shift reactor by the injection of water. Additional steam raising and the addition of steam would be an alternative to water injection.

The water gas shift reaction is exothermic and in order to recover the heat of reaction effectively, the low temperature shift reactor 236 is constructed as a tubular steam-raising, isothermal reactor. The

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favorable low reaction temperature within catalyst filled tubes 238 of the reactor 236 is maintained by raising steam from water flow from the drum 229. Alternatively, the CPO reactor effluent, which has a

5 high concentration of carbon monoxide, could be passed through a high temperature shift reactor, and the resulting higher concentration of carbon monoxide could be accepted or the high temperature shift could be followed by a low temperature shift, or the CPO reactor

10 effluent could be passed through a multibed low temperature shift reactor with interbed cooling.

The plant illustrated in Fig. 12, employs the common steam drum 229 for the CPO boiler 228 and the low temperature steam raising tubular shift reactor

15 236. Output 240 of the steam drum 229 provides the steam 216 for mixing with the feedstock as well as providing steam in line 242 which is passed through coil 244 of the heater 204 to produce superheated steam 246 which can be used to drive turbines, or be used for

20 any other purpose.

Layout or other plant process considerations may cause the employment of separate steam drums to be more cost effective. Efficiency improvement may also be obtained by using a separate steam drum for the CPO

25 boiler and raising steam at a higher pressure. The use of a high temperature shift catalyst would also allow the exothermic heat of reaction of the shift reaction to be recovered as higher pressure steam. Alternatively to the preheating of air and feedstock and the

30 superheating of steam in the fired heater, such preheating and superheating can be carried out by heat exchange with the CPO effluent downstream from the reactor 100.

The output 250 of the low temperature shift reactor 236 is passed through heat exchanger 252 which heats boiler feed water stream 254, through line 256 to heat exchanger 258 which preheats water stream 260, through line 262 to water cooled condenser 264, and then through line 266 to knockout drum 268 where condensed water 270 is separated from the gas stream 272. The condensate 270 together with make-up demineralized water 274 form the water stream 260 which, after passing through the heater 264, passes through line 276 to deaerator 278 where air and dissolved gases are removed. Steam input 280 to column section 282 of the deaerator 278 assists in removal of dissolved gases. A portion of the steam input 280 is supplied over line 284 from the steam line 240, and the remaining portion is supplied from gas output 286 of blowdown drum 288 receiving blowdown stream 290 from the steam drum 229. Deaerated water 302 is raised in pressure by pump 304 to line 306 which forms the spray feed 232 and the boiler feed 254.

The separated gas stream 272 from the separator 268 is passed to a hydrogen recovery or purification unit 292 in which hydrogen product stream 294 is separated from waste gas stream 296 passing to surge drum 298 which supplies the waste fuel 206 and excess waste fuel 300. The waste fuel will typically have a low calorific value which is not suitable for combustion in a conventional burner, and so the burner for heater 204 is an "adiabatic combustor" or a catalytic combustor with the flue gases heating the process stream coils in a convection heat transfer duct. A fuel pressure of 5 to 10 psig (34 to 68 KPa) is sufficient for the adiabatic combustor and the catalytic combustor. Alternatively, natural gas is

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mixed with the waste fuel and a duct type burner with a natural gas pilot is used to combust the mixture with air. The hydrogen recovery unit 292 is a pressure swing adsorption (PSA) unit, cryogenic separation unit, or prism separation unit.

Pressure swing adsorption involves the adsorption of components to be removed at high pressure followed by their desorption at low pressure. The process operates on a repeated cycle having two basic steps, adsorption and regeneration. Not all the hydrogen is recovered as some is lost in the waste gas during the regeneration stage. By careful selection of the frequency and sequence of steps within the cycle however, the recovery of hydrogen is maximized. Regeneration of the adsorbent is carried out in three basic steps. First, the adsorber is depressurized to the low pressure. Some of the waste components are desorbed during this step. Second, the adsorbent is purged at low pressure, with the product hydrogen removing the remaining waste components. Thirdly, the adsorber is repressurized to adsorption pressure ready for service. A typical pressure swing adsorption system suitable for the present process is available under the trademark "Hy Siv" from Union Carbide. Such a system may include up to ten individual beds. At any one time three of the vessels would be in the adsorption stage and the other seven vessels would be in various stages of regeneration.

A cryogenic separation unit first removes carbon dioxide by conventional bulk carbon dioxide removal techniques prior to cryogenic separation of hydrogen. Final traces of carbon dioxide and water vapor must be removed in a molecular sieve unit in order to prevent blockage of the cold box by solidification of these

components. From the molecular sieves, the feed gas is cooled by returning product hydrogen and fuel gas streams to condense nitrogen, methane and carbon monoxide before being let down in an expansion turbine to approximately 30 psig (210 KPa). After reheating, by cooling the inlet stream, the product hydrogen is recompressed to the required pressure in a centrifugal compressor. The condensed gases are let down to fuel gas pressure and also used to cool the incoming feed gas before being passed to the fired heater for use as fuel. The fuel gas is available at approximately 20 psig (140 KPa).

A prism separation unit makes use of the principle of selective permeation through membranes. Permeation of gas molecules through a membrane is in two stages, the first being dissolution into the membrane structure and the second being diffusion through the membrane. With a mixture of gases, different components will permeate at different rates, even when the partial pressure driving forces are equal. The hollow-fiber membrane consists of a porous asymmetric polymer substrate and a polymer coating of high permeability. The selective permeation characteristics of the system allow faster gases such as water vapor, hydrogen and carbon dioxide to be separated from the slower gases such as methane, nitrogen, argon, oxygen, carbon monoxide and hydrocarbons. The faster gases permeate through the hollow fiber and are removed at a low pressure while the slower gases concentrate upstream of the membrane and are removed essentially at inlet pressure. As carbon dioxide and hydrogen both permeate the membrane at similar speeds, it is necessary to remove carbon dioxide by a bulk carbon dioxide removal method prior to passing the gases to the prism separators.

The operating pressure is too low to achieve efficient hydrogen recovery and the feed gas must therefore be compressed to approximately 575 psig (3960 KPa) before being passed to the separators. The product from the first separator stage is available at 100 psig (689 KPa) but the purity is low. Recompression to 625 psig (4310 KPa) and a second stage of prism separation is therefore necessary to yield the final product at about 200 psig (1380 KPa).

The process of the invention can be further understood with reference to the following examples, which are intended to illustrate the invention and are not intended to limit its scope in any way.

EXAMPLE I

Natural gas is converted to synthesis gas in a catalytic partial oxidation reactor of the construction shown in Fig. 1. There are included nine catalyst discs 54, each having a diameter of 30 inches (0.76m) and a thickness of 10 inches (0.25m). The discs are formed from a honeycomb monolith of cordierite material with a geometric surface area of approximately 25 cm²/cm³. A high surface area alumina layer is deposited on the cordierite to serve as a support upon which finely dispersed catalytic metal components are distended. The catalytic metal components are approximately 50% by weight platinum and 50% by weight palladium. Space velocity of the catalyst is 97,000 hr.⁻¹

Natural gas (>95% methane) is mixed with steam at various steam-to-carbon molar ratios, heated and supplied through 10-inch (25.4 cm) diameter inlet 66 at a pressure of 400 psig (2760 KPa). Oxygen containing gas is heated and supplied through two 8-inch (20.3 cm) inlets 70 at a pressure of 410 psig (2830 KPa). The

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diameter of the lower portion 76 of the chamber 72 is 27 inches (0.68m) with the diameter of the upper portion 74 being 36 inches (0.91m). There are 261 tubes 80 having 0.5 inch (12.7mm) internal diameters and having lengths of 20 inches (0.51m). Six orifices 86 of 0.123-inch (3.12 mm) diameter are formed in each tube with four of the orifices evenly spaced around each tube at a distance of 4 inches (0.102m) above the lower end of the tube and with the remaining two orifices formed opposite each other at a distance 6 inches (0.152m) above the lower end of the tube. The bottom member 78 has a thickness of 5 inches (0.127m) and the passageway sections 84 are conical with upper diameters of 0.5 inches (12.7 mm) and lower diameters of 1.75 inches (44.5mm). Pressures within the chambers 68 and 72 are maintained at essentially the inlet pressures.

The temperature of the mixed reactant gases is 1,100°F (593°C). Fig. 7 shows oxygen consumption for the catalytic partial oxidation process, as a function of steam-to-carbon molar ratio, for reaction temperatures of 1,600°F (870°C), 1,750°F (950°C) and 1,900°F (1040°C) and an operating pressure of 400 psig (2760 KPa). It can be seen from the graph that oxygen consumption, expressed as oxygen-to-carbon molar ratio, is relatively low for the process of the invention as compared with present commercial partial oxidation processes. The dashed line 25 in Fig. 8 represents the conditions under which carbon deposits are formed.

Fig. 8 shows the molar ratio of hydrogen, as H_2 , to carbon monoxide in the product as a function of steam-to-carbon ratio for reaction temperatures of 1,600°F (870°C), 1,750°F (950°C) and 1,900°F (1040°C).

Figs 9 and 10, respectively, show the amounts of methane and carbon dioxide, as volume %, in the product as a function of steam-to-carbon ratio for reaction temperatures of 1,600°F (870°C), 1,750°F (950°C) and
5 1,900°F (1040°C).

Fig. 11 shows the effective H₂ production of the process, expressed as total moles of H₂ and carbon monoxide in the product divided by total moles of H₂ and carbon in the feedstock.

10

Example II

An example of the process performed by the hydrogen plant of Fig. 12 is illustrated in the following TABLES I, II and III which contain mole/hour, mole percent, and parameters of pressure, temperature,
15 water/steam flow, and heat transfer for the process. The moles/hour are lb moles/hour (0.4563 kg moles/hour). The example employs pressure swing adsorption fo the hydrogen recovery unit 292 to produce the hydrogen product from the synthesis gas.

TABLE I
Moles / Hour

DESCRIPTION	CO	CO2	H2	CH4	N2	Ar	O2	C2H6	C3H8	C4H10	H2O	TOTALS
Natural Gas (line 200)		0.53		877.08	0.88			0.97	0.28	0.08		879.81
Oxygen (line 224)						2.35	467.15					469.50
CPO in (lines 222 & 224)		0.53		877.08	0.88	2.35	467.15	0.97	0.28	0.08	880.16	2228.46
CPO out (line 226)	646.45	187.23	1750.10	47.00	0.88	2.35					784.81	3428.81
LT Shift in (line 234)	646.45	187.23	1750.10	47.00	0.88	2.35					1317.00	3851.01
LT Shift out (line 250)	9.7	823.98	2386.85	47.00	0.88	2.35					680.24	3851.01
Waste fuel (line 206)	6.46	548.30	127.10	31.28	0.58	1.56					7.54	722.83
Air (line 208)					584.05		155.22				9.13	748.40
Flue gas (204)		586.04			584.64	1.56	25.88				206.35	1404.47
Condensate (line 270)		0.25									668.91	669.16
PSA extra (line 300)	3.24	275.43	83.85	15.72	0.28	0.78					3.78	383.11
Deaerator vent (283)		0.25									15.76	16.01
Hydrogen product (294)			2185.80									2185.80

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TABLE II
Mole Percent

DESCRIPTION	CO	CO2	H2	CH4	N2	Ar	O2	C2H6	C3H8	C4H10	H2O
Natural Gas (line 200)		0.06		99.69	0.10			0.11	0.03	0.01	
Oxygen (line 224)						0.5	99.5				38.49
CPO in (lines 222 & 224)		0.02		38.34	0.04	0.11	20.85	0.04	0.01		23.18
CPO out (line 226)	18.85	5.48	51.04	1.37	0.03	0.07					33.33
LT Shift in (line 234)	16.36	4.74	44.30	1.19	0.02	0.06					17.22
LT Shift out (line 250)	0.25	20.85	60.41	1.19	0.02	0.06					1.04
Waste fuel (line 206)	0.89	75.86	17.58	4.33	0.08	0.22					1.22
Air (line 208)					78.04		20.74				14.88
Flue gas (204)		41.73			41.83	0.11	1.84				99.86
Condensate (line 270)		0.04									1.04
PSA extra (line 300)	0.89	75.86	17.58	4.33	0.08	0.22					98.44
Deaerator vent (283)		1.56									
Hydrogen product (294)			100.00								

TABLE III
Parameters

DESCRIPTION	Pressure		Temperature		Water/Steam		Net Heat Transfer	
	PSIG	Kpa	DEG F	DEG C	LBS/HR	KG/HR	MMBTU/HR	KG CAL 10 ⁶ /HR
Natural Gas 200	350	2410	80	27			2.82	0.71
Coil 202								
Waste Fuel 206	5	34	100	38				
Combustion Air 208			80	27				
Heated Feedstock 210	340	2340	400	204	15857	7193		
Steam 216								
Feedstock & Steam 218			388	198			14.35	3.62
Coil 220								
CPO Feedstock 222	310	2140	1100	593				
Oxygen 224	335	2310	300	150				
CPO Effluent 226	300	2070	1750	954			27.20	6.85
CPO Boiler 228								
Steam Drum 229	400	2760	648	211				
Process Line 230	295	2030	800	427				
Water Spray 232	500	3450			8412	3816		
Process Line 234	285	1970	418	214	43354	19665		
Steam Out 240							5.0	1.26
Coil 244								
Superheated Steam 246	385	2650	825	441	26691	12107		
Shift Reactor Out 250	280	1930	464	240			7.88	1.99
Heat Exchanger 252								
Boiler Feed 254			400	204	44221	20058		
Process Line 256			270	132			5.9	1.49
Heat Exchanger 258								
Process line 262			236	113				
Condenser 264							8.82	2.22
Process Line 266	280	1930	100	38				

TABLE III (CONTINUED)
Parameters

DESCRIPTION	Pressure		Temperature		Water/Steam		Net Heat Transfer MMBTU/HR	KG CAL 10 ⁶ /HR
	PSIG	KPa	DEG F	DEG C	LBS/HR	KG/HR		
Deminerlized Water 274	40	276	100	38	40888	18546		
Water 276			210	99				
Deaerator 278	5	34	228	109				
Steam 284					806	366		
Blowdown Vapor 286	15	103	250	121	182	83		
Blowdown Stream 290					867	393		
Hydrogen Product	250	1720	100	38				
PSA Waste 296	5	34	100	38				
Deaerated Water 302					53633	24328		
Pump Out 306	500	3450						

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5 Since many modifications, variations and changes in detail may be made in the above described embodiments without departing from the scope and spirit of the invention, it is intended that all matter described in the foregoing description and shown in the accompanying drawings be interpreted as illustrative and not in a limiting sense.

Claims

1. A process for producing a hydrogen-rich gas from hydrocarbonaceous feedstock which comprises:

- 5 (a) introducing to a catalytic partial oxidation zone an essentially completely mixed gaseous mixture of a hydrocarbonaceous feedstock, oxygen or an oxygen-containing gas and, optionally, steam in which the steam-to-carbon molar ratio is from 0:1 to 4.0:1 and the oxygen-to-carbon molar ratio is from 0.4:1 to 10 0.8:1, said mixture being introduced to a catalytic partial oxidation zone at a temperature not lower than 200°F (93°C) below its autoignition temperature;
- 15 (b) partially oxidizing the hydrocarbonaceous feedstock in the catalytic partial oxidation zone at a temperature equal to or greater than a minimum non-carbon-forming temperature selected as a linear function which includes a range from 1600°F (870°C) to 1900°F (1040°C) corresponding to a range of the steam-to-carbon molar ratio from 0.4:1 to 0:1 to produce a 20 gas consisting essentially of methane, carbon oxides, hydrogen and steam by passing the mixture through a catalyst capable of catalyzing the oxidation of the hydrocarbons, said catalyst having a ratio of geometric surface area to volume of at least 5 cm²/cm³ and a 25 volume sufficient to produce a space velocity in the range from 20,000 hour⁻¹ to 500,000 hour⁻¹ thereby producing synthesis gas containing hydrogen, carbon monoxide and carbon dioxide; and
- 30 (c) separating hydrogen in the synthesis gas to produce a hydrogen product stream.

2. A process as claimed in claim 1 wherein a proportion of the carbon monoxide in the synthesis gas is converted to carbon dioxide by a water gas shift

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reaction with the reactants in contact with a shift catalyst.

5 3. A process as claimed in claim 1 wherein the carbon dioxide is removed from the synthesis gas in the separation step by pressure swing adsorption.

 4. A process as claimed in claim 2 wherein the carbon dioxide is removed from the synthesis gas in the separation step by pressure swing adsorption.

10 5. A process as claimed in claim 1, wherein the steam-to-carbon molar ratio is from 0.3:1 to 3.0:1.

 6. A process as claimed in claim 1, wherein the steam-to-carbon molar ratio is from 1.0:1 to 2.0:1.

15 7. A process as claimed in claim 1, wherein the shift gas catalyst is contained in a tubular reactor which uses the exothermic heat of reaction to generate steam.

 8. A process as claimed in claim 1, wherein the oxygen-containing gas is an oxygen-rich gas containing at least 70 mol. % oxygen.

20 9. A process as claimed in claim 1, wherein the oxygen-containing gas is an oxygen-rich gas containing at least 90 mol. % oxygen.

 10. A process as claimed in claim 1 wherein the carbon dioxide is removed by contacting the gas with a countercurrent liquid stream of carbon dioxide absorbing medium.

25 11. A process as claimed in claim 1, which further comprises removing nitrogen from the gas stream.

30 12. A process as claimed in claim 11, wherein nitrogen is removed by pressure swing absorption.

 13. A process as claimed in claim 11, wherein nitrogen is removed by cryogenic separation.

14. A process as claimed in claim 11, wherein nitrogen is removed by prism membrane separation.

SUBSTITUTE SHEET

1/10

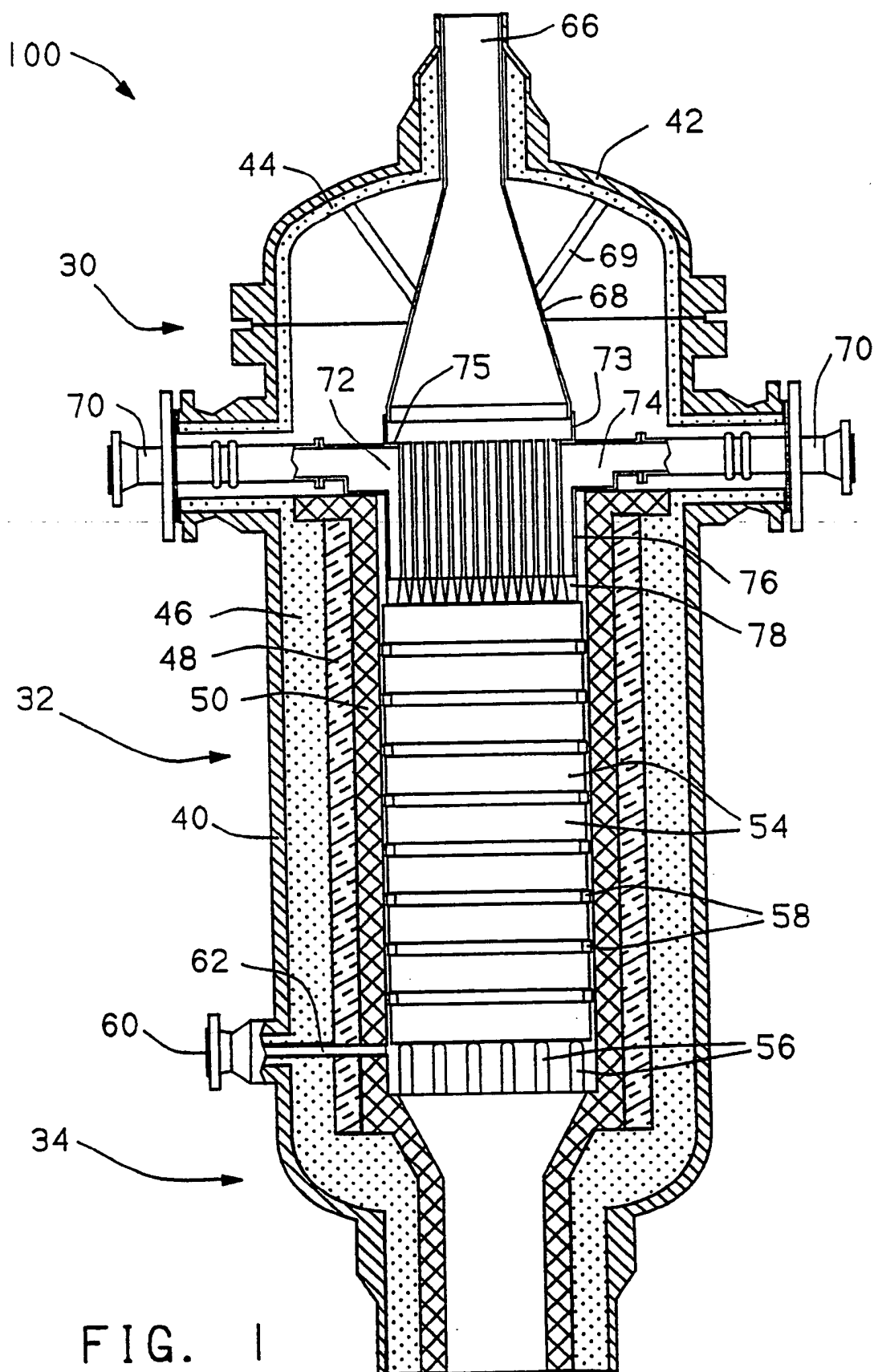


FIG. 1

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2/10

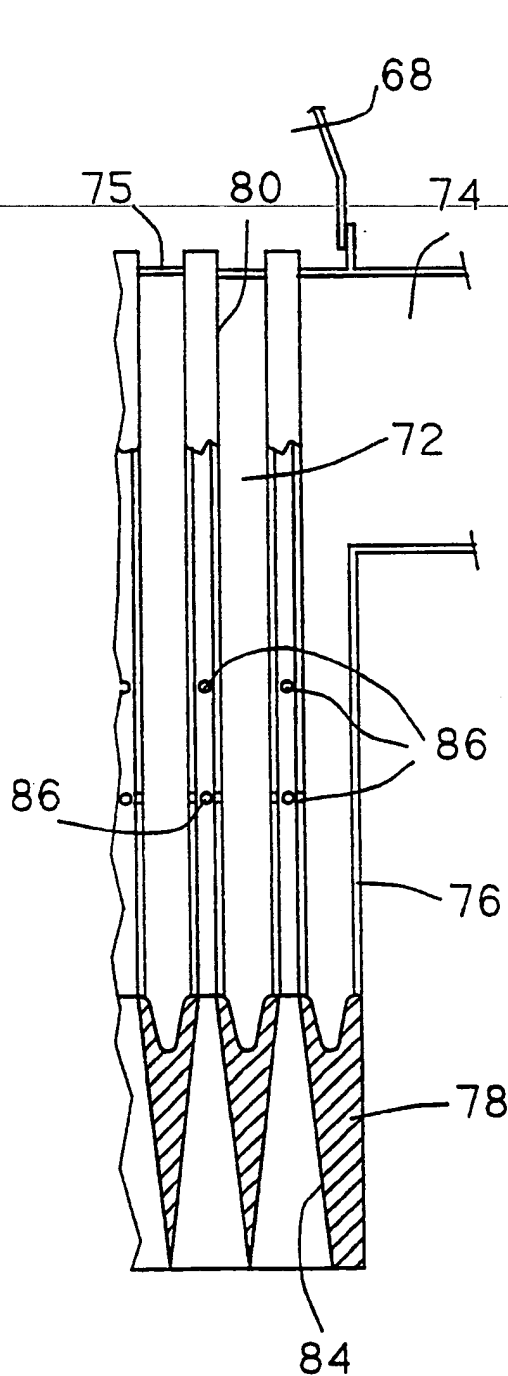


FIG. 2

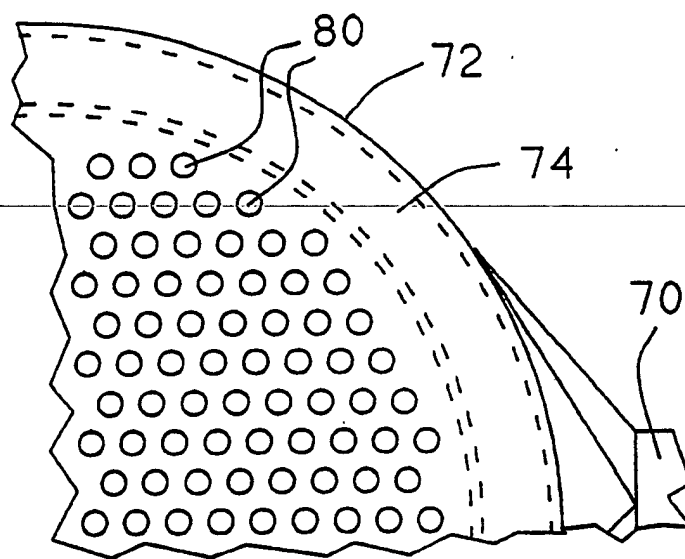


FIG. 3

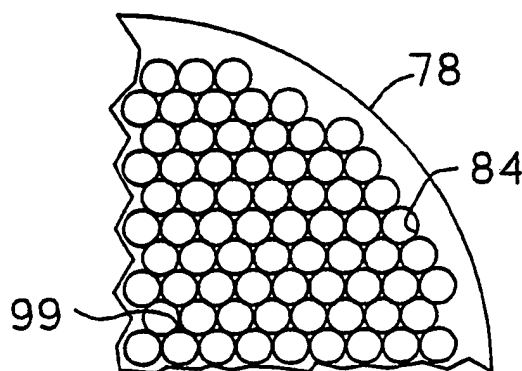
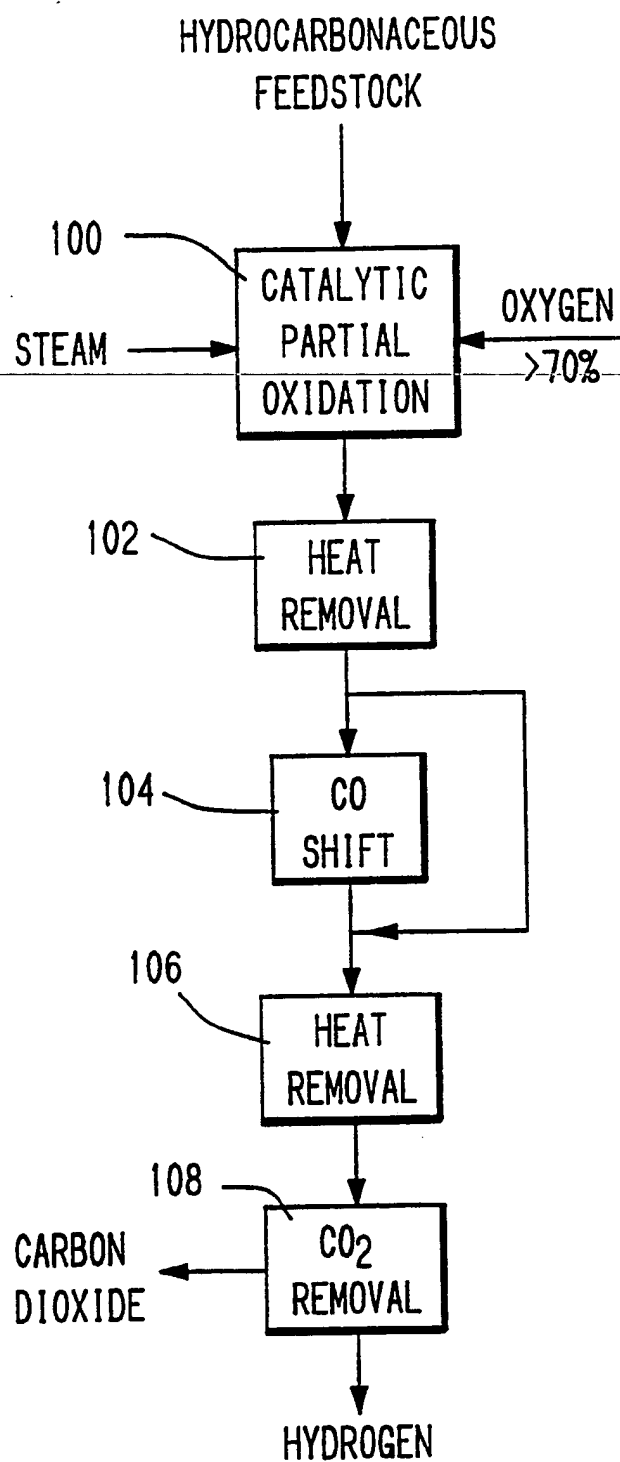


FIG. 4

4/10



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FIG. 6

5/10

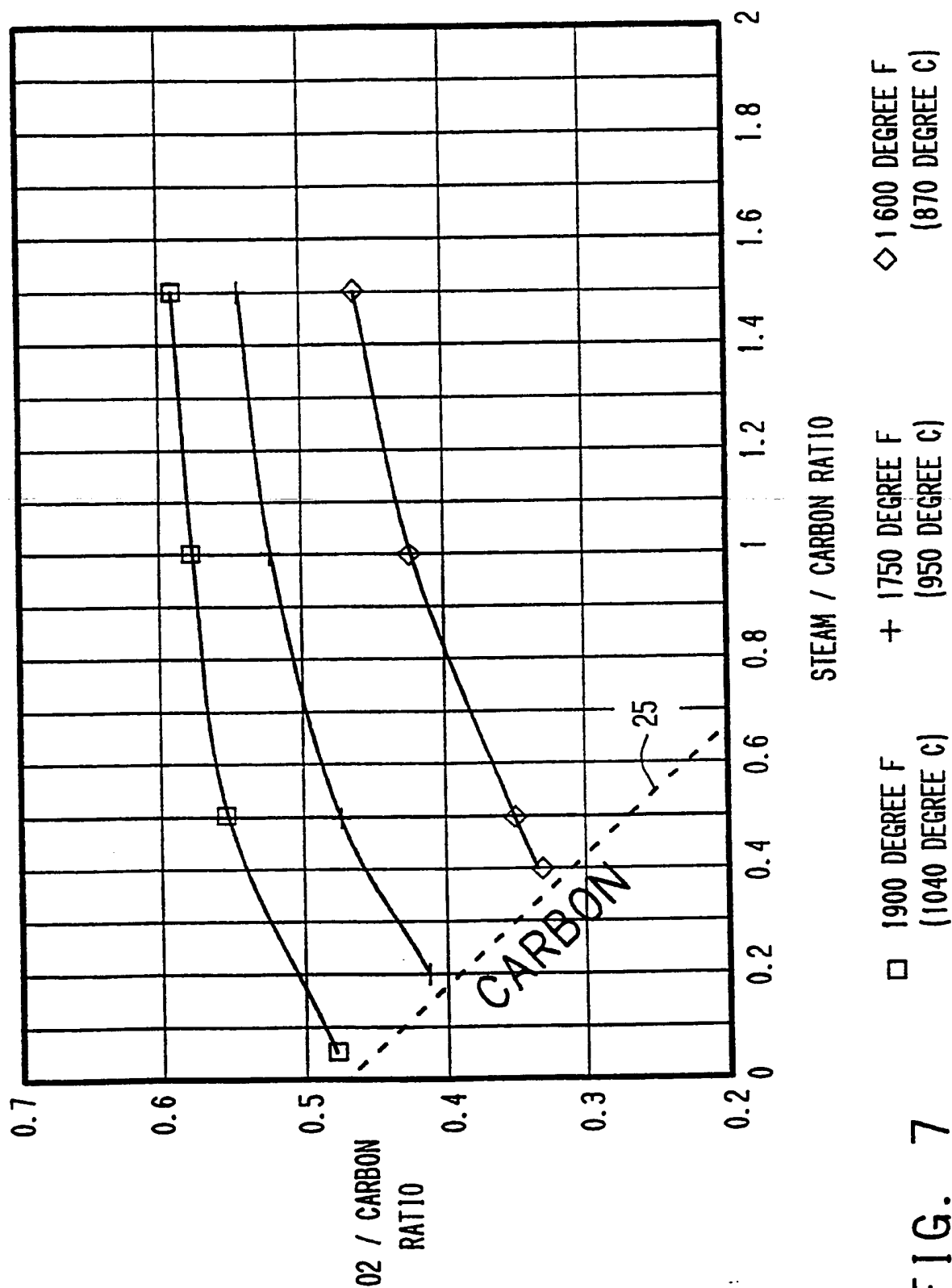


FIG. 7

SUBSTITUTE SHEET

6/10

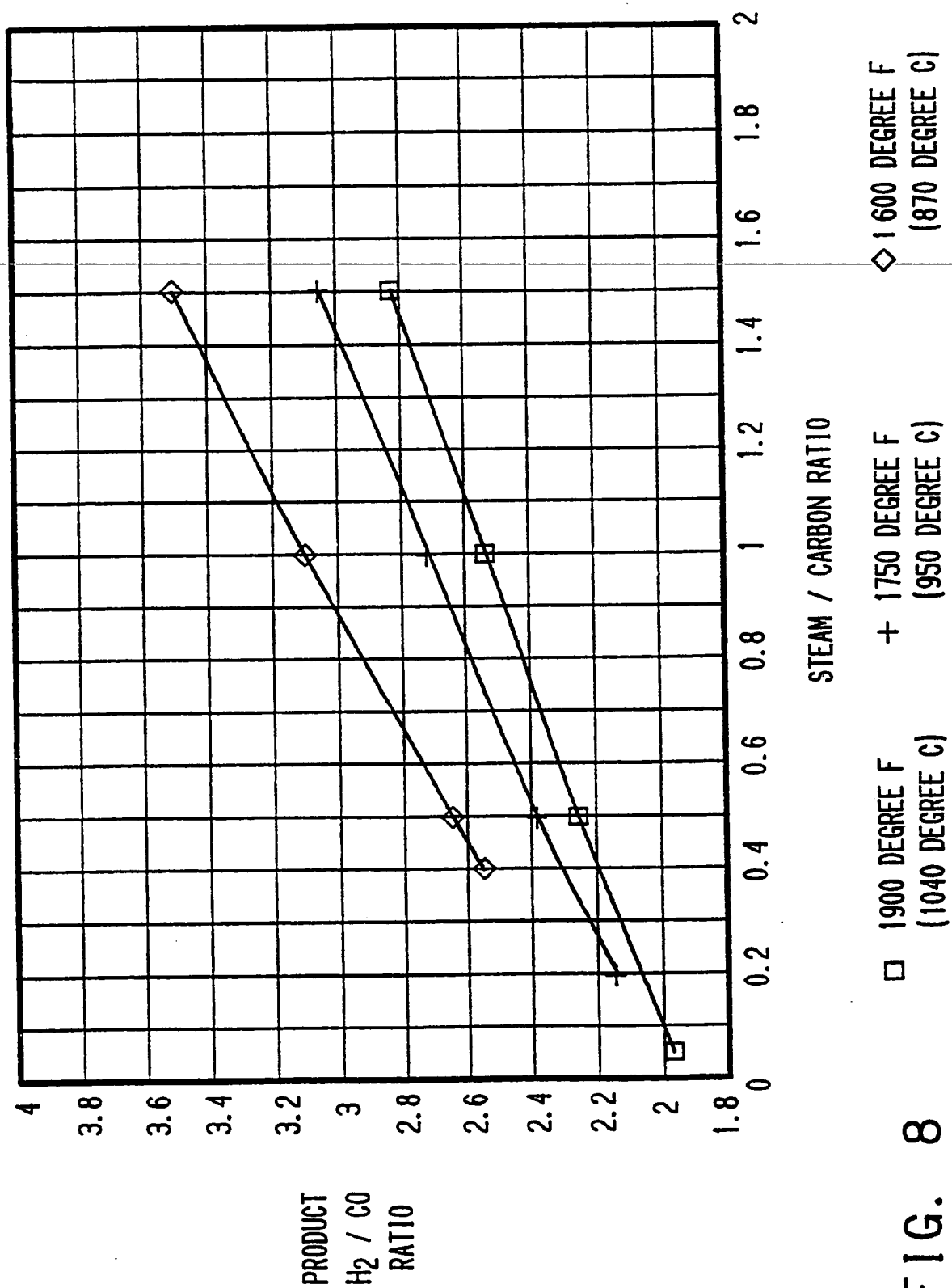


FIG. 8

SUBSTITUTE SHEET

7/10

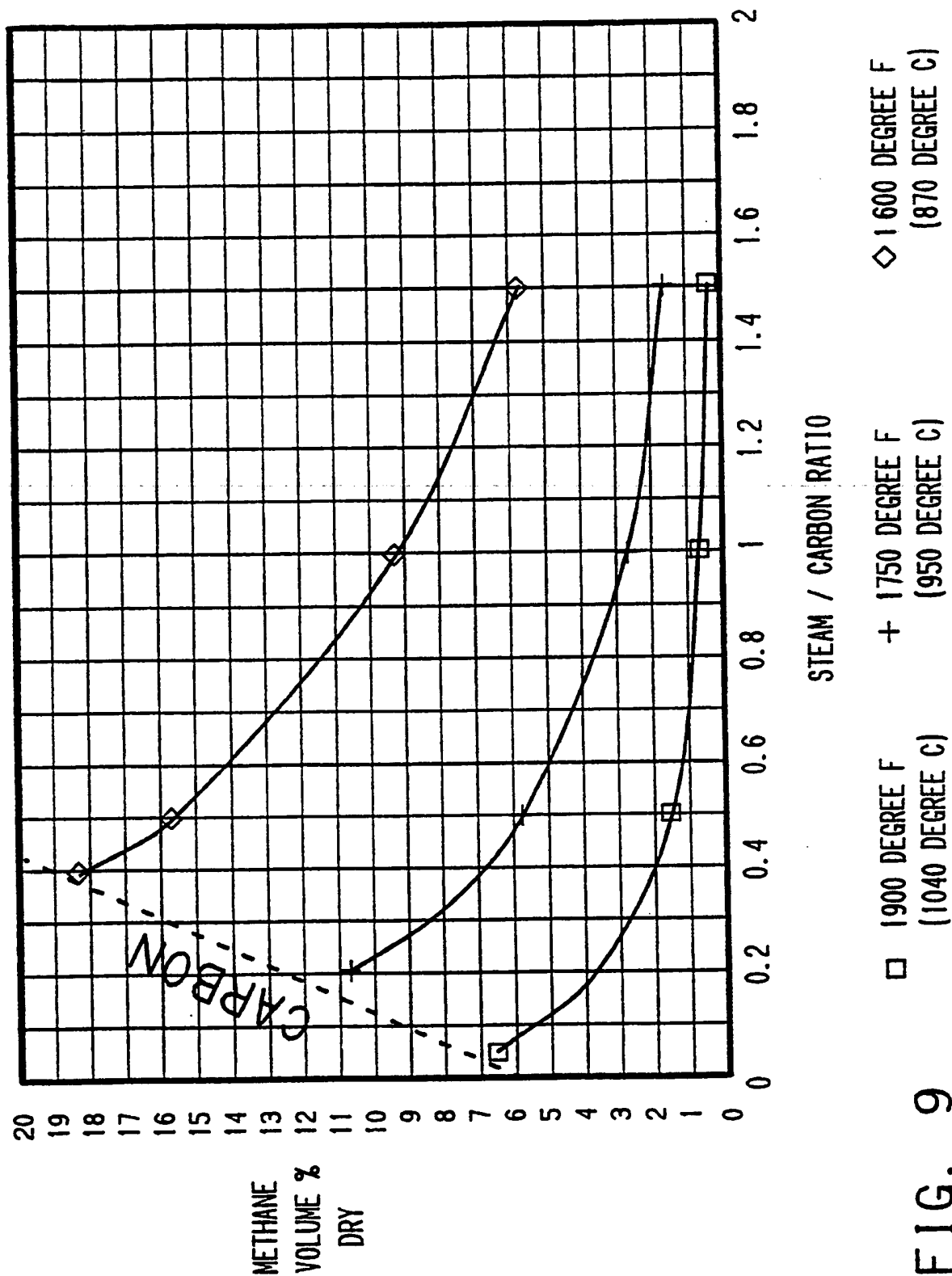


FIG. 9

SUBSTITUTE SHEET

8/10

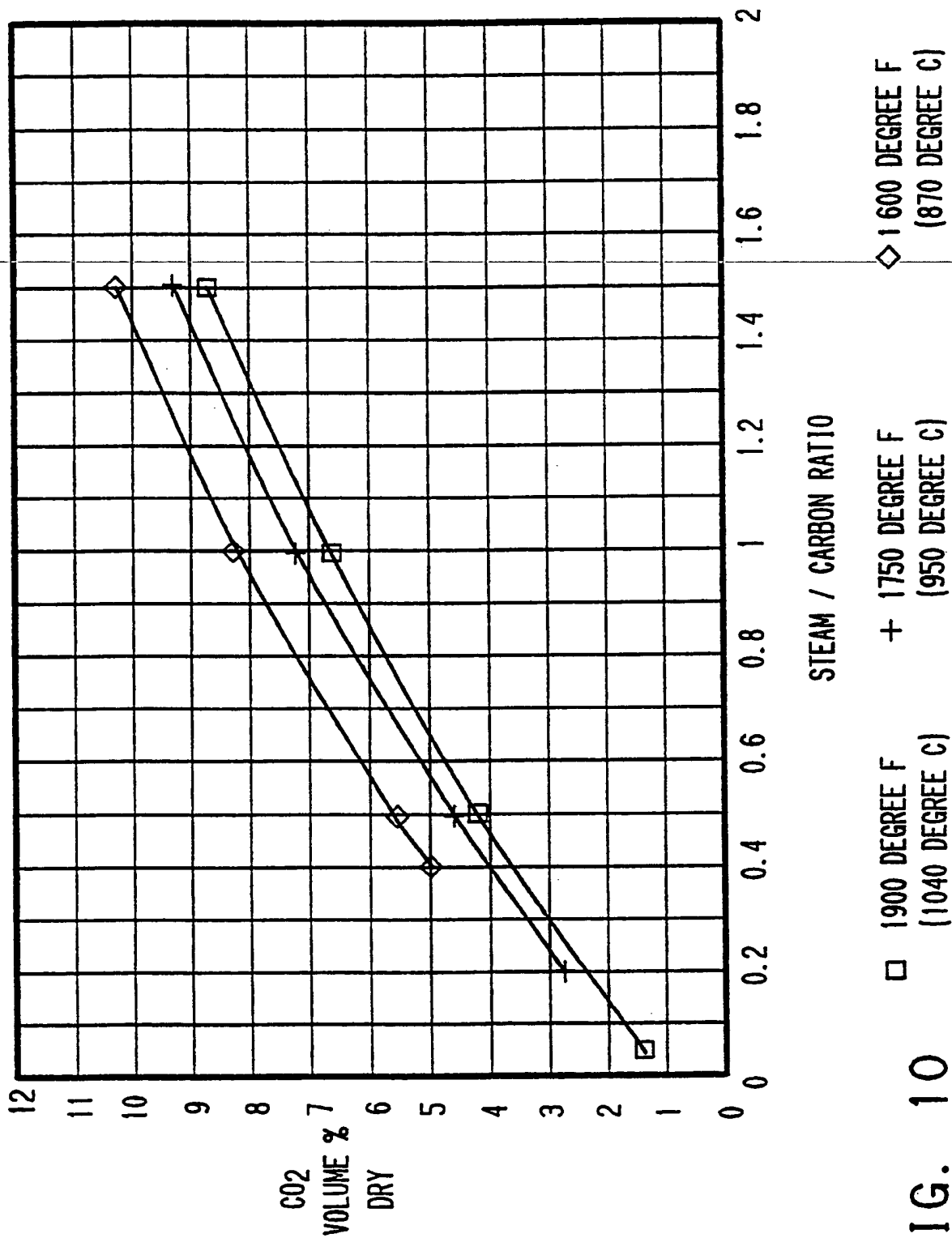


FIG. 10

9/10

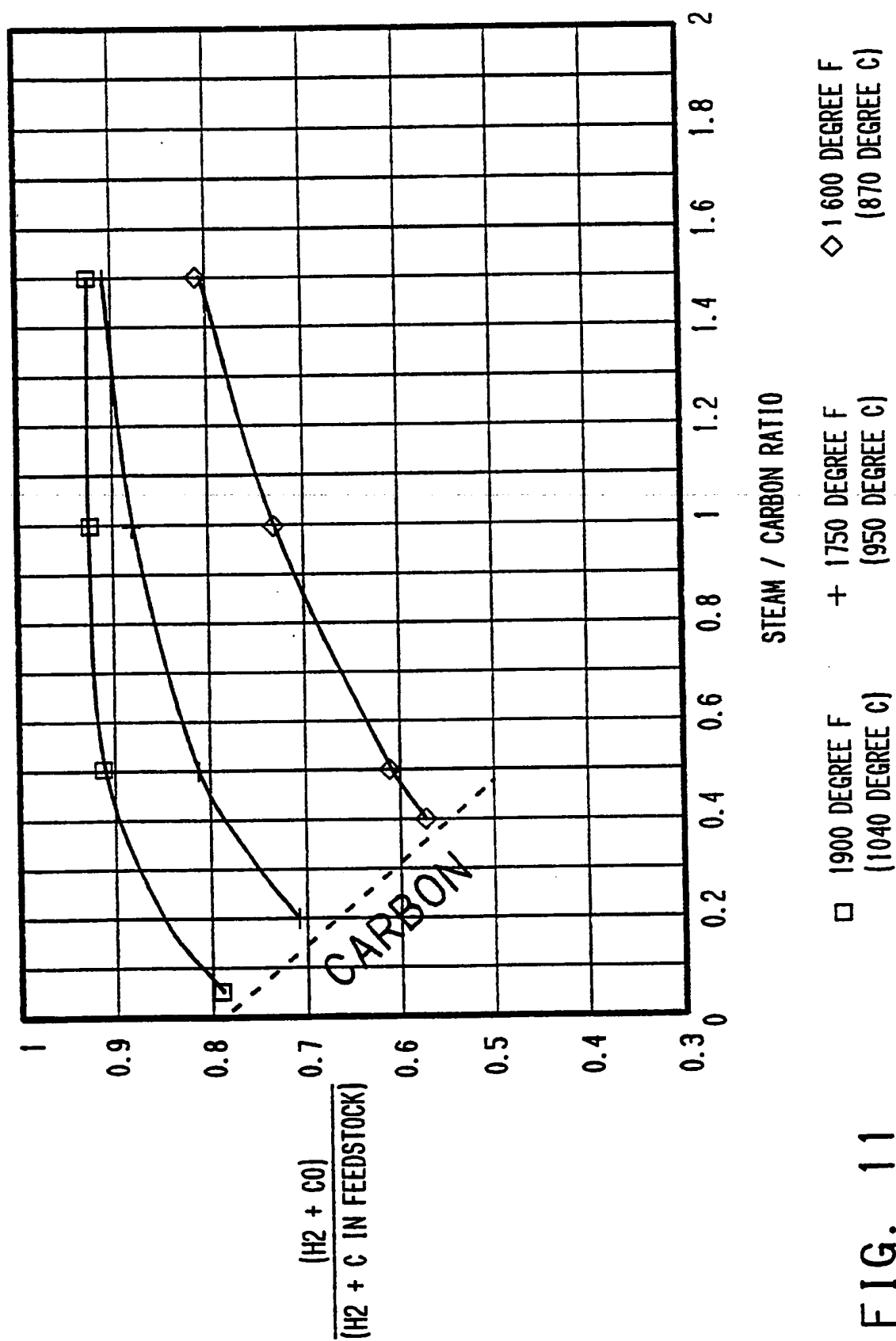


FIG. 11

SUBSTITUTE SHEET

10/10

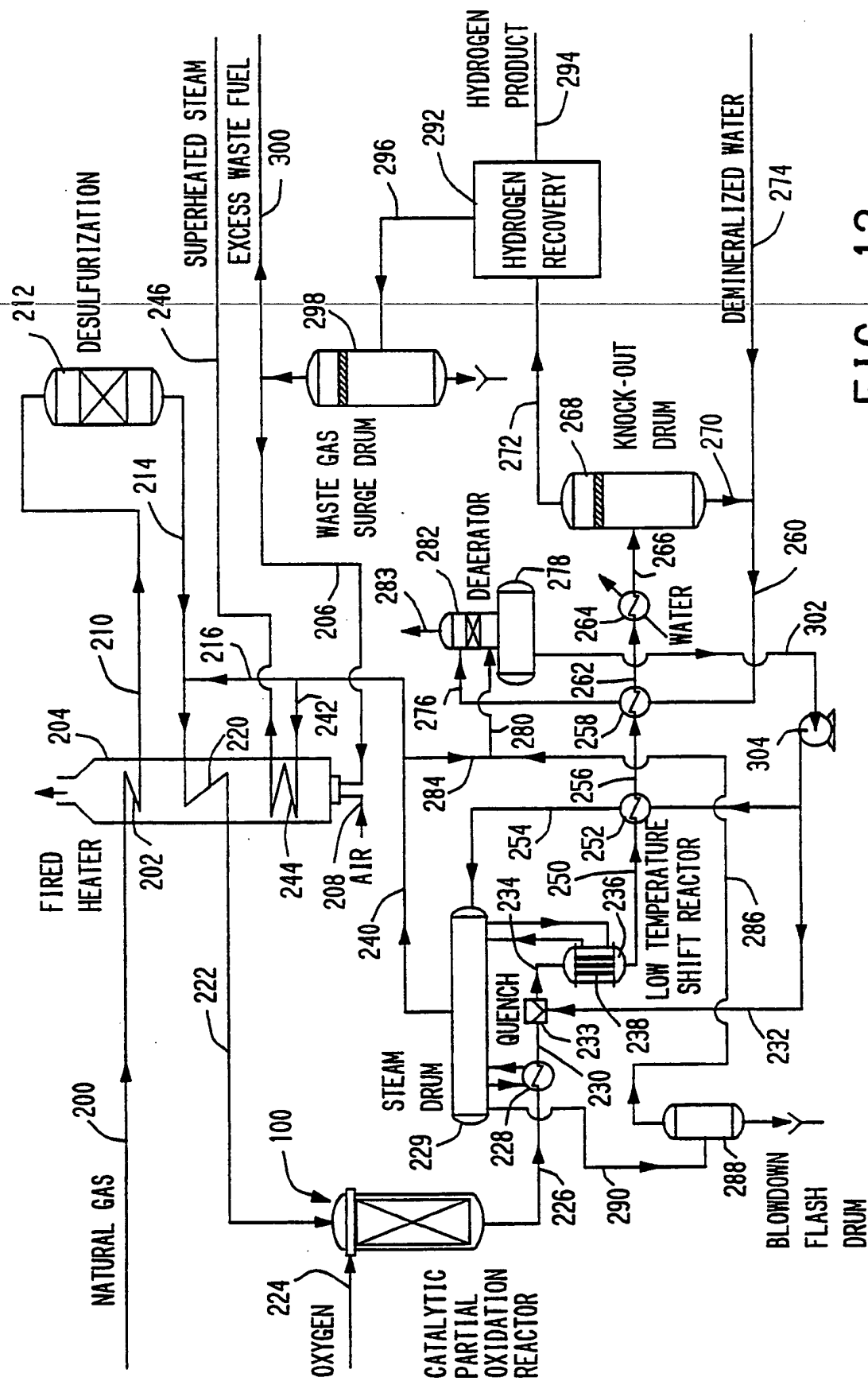


FIG. 12

INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US 89/05369**

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 01 B 3/38

II. FIELDS SEARCHED

Minimum Documentation Searched

Classification System

Classification Symbols

IPC5

C 01 B

Documentation Searched other than Minimum Documentation
(If such Documents are included in the fields searched)

III. DOCUMENTS CONSIDERED TO BE RELEVANT

Category * Citation of Document, ** with indication, where appropriate, of the relevant passages ** Relevant to Claim No. **

X	EP, A2, 0112613 (ENGELHARD CORPORATION) 4 July 1984, see page 5, line 15 - line 25; page 6, line 5 - line 10; page 14, line 19 - line 23; page 16, line 5 - line 8 page 17; page 67, line 7 - line 14; page 69, line 13 - line 17; claims 1, 3, 4, 5, 13	1,2,8,9
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Y		1,2,3, 10,11, 12
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X	EP, A1, 0262947 (JOHNSON MATTHEY PUBLIC LIMITED COMPANY) 6 April 1988, see page 2, line 49 - line 63	1
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* Special categories of cited documents: 10

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

7th March 1990

Date of Mailing of this International Search Report

21. 03. 90

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

T.K. WILLIS

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category*	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	US, A, 3377138 (WILLIAM R. GUTMANN ET AL) 9 April 1968, see claim 1 --	2,10
Y	WO, A1, 87/02347 (UNION CARBIDE CORPORATION) 23 April 1987, see claims 1, 4, 11, 15, 17 --	2,3,11, 12
X,P,L	EP, A2, 0303438 (DAVY MCKEE CORPORATION) 15 February 1989, see the whole document --	1-14
A, P	EP, A2, 0303439 (DAVY MCKEE CORPORATION) 15 February 1989, see the whole document --	1-14
A	DE, A1, 2352438 (THE BRITISH PETROLEUM CO., LTD.) 24 April 1975, see the whole document --	1
A	US, A, 2465235 (N.F. KUBICEK) 22 March 1949, see the whole document -- -----	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

PCT/US 89/05369

SA 32934

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EIPP file on 08/11/89
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		CA-A- 1217504	03/02/87
		AU-A- 572797	19/05/88
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		CA-A- 1210567	02/09/86
		US-A- 4483691	20/11/84
		CA-A- 1210242	26/08/86
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		JP-A- 1159037	22/06/89
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US-A- 2465235	22/03/49	NONE	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82